

Carbon nanotubes,  
lipid bilayers,  
salt solutions,  
real metals,  
Forces from across the spectrum

Adrian Parsegian and many friends:

Roger French (Dupont), Rudi Podgornik  
(NIH, Slovenia), Rick Rajter (MIT), Wai-Yim  
Ching (UMKC) ; Horia Petrache (IUPUI) et al.  
[parsegian@physics.umass.edu](mailto:parsegian@physics.umass.edu)

“Van der Waals”

“Casimir”

“Lifshitz”

“Dzyaloshinskii Lifshitz Pitaevskii DLP”

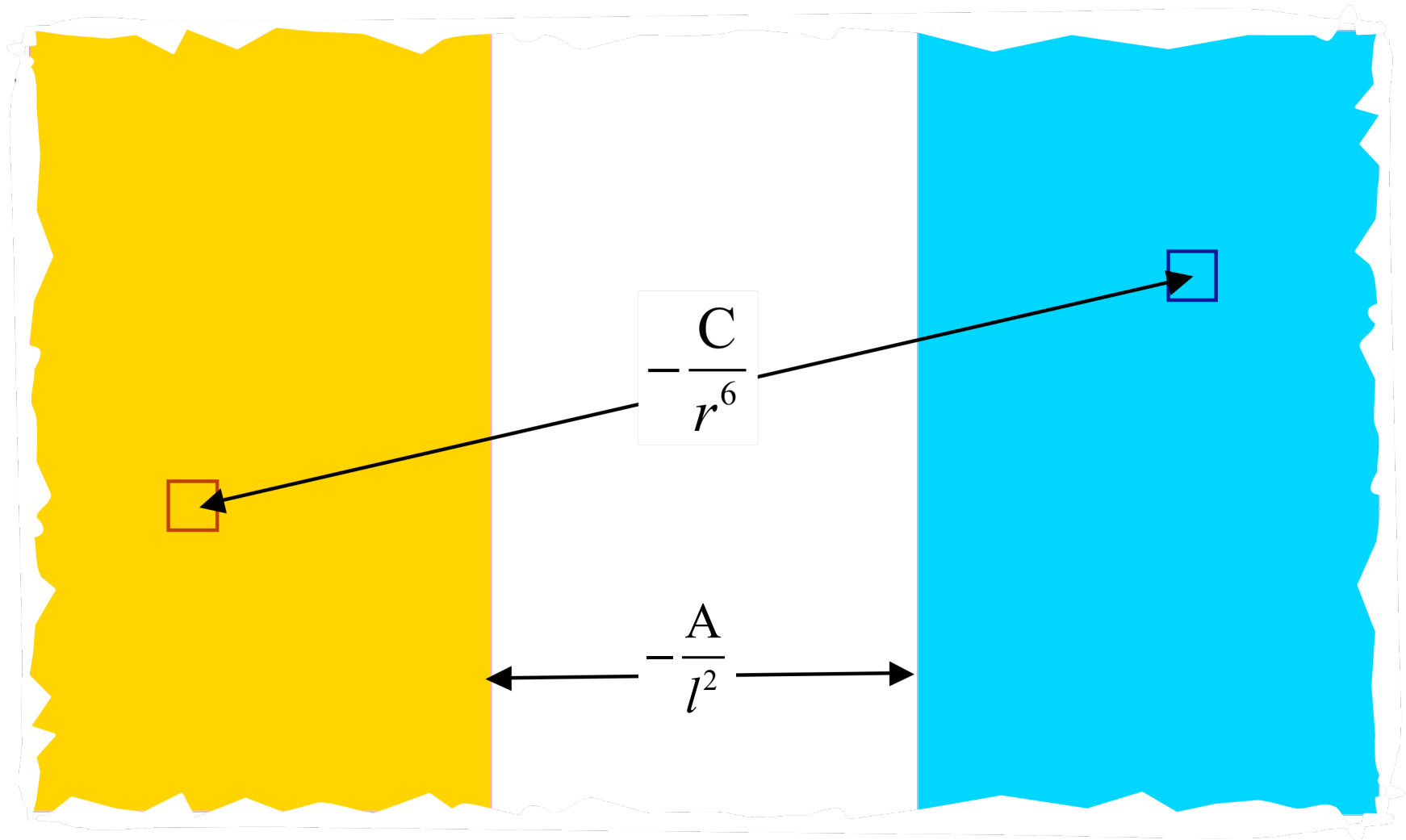
“electrodynamic”

field/charge-fluctuation forces:

The spectrum of possibilities

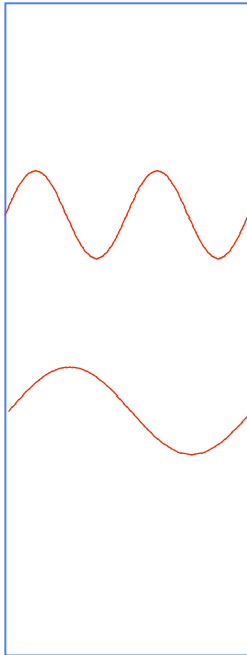
space, time, and temperature

Pairwise summation of dipole interactions  
in condensed media (Derjaguin, 1934, Hamaker, 1937)

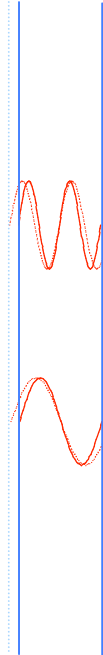


# Modern, macroscopic point of view

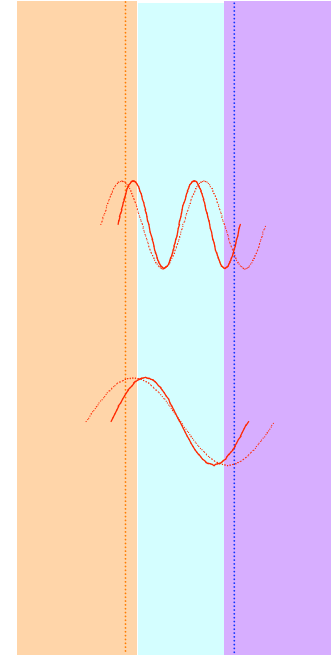
## Focus on electromagnetic waves



Planck (1890's):  
Hollow "black" box



Casimir (1940's):  
Parallel flat ideally  
conducting  
surfaces, vacuum.



Dzyaloshinskii , Lifshitz  
& Pitaevski (1950's):  
Any two flat surfaces of  
any materials



Not so modern!  
c.f. Ph.D. thesis (1894) of P.N. Lebedev:

Hidden in Hertz's research, in the interpretation of light oscillations as electromagnetic processes, is still another as yet undealt with question, that of the source of light emission of the processes which take place in the molecular vibrator at the time when it give up light energy to the surrounding space; such a problem leads us [...] to one of the most complicated problems of modern physics -- the study of molecular forces.

Of greatest interest and of greatest difficulty is the case of a physical body in which many molecules act simultaneously on one another, the vibrations of the latter not being independent owing to their close proximity.

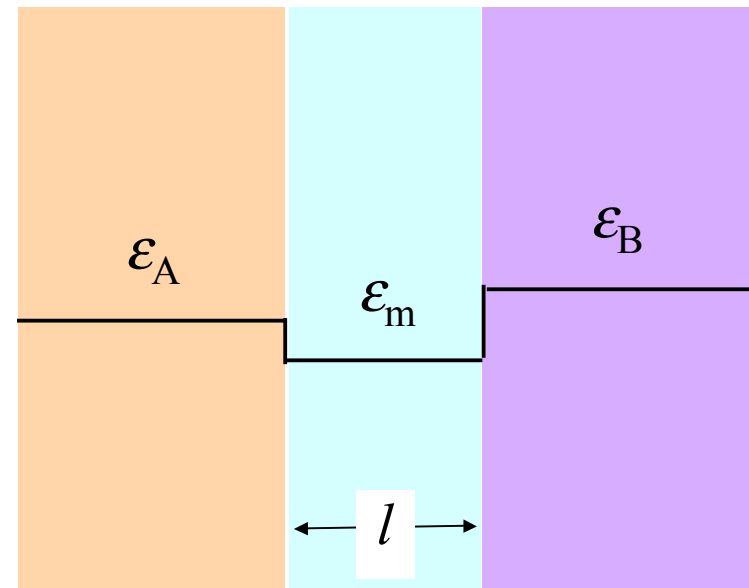


Recall simplest form of DLP interaction energy:  
half-spaces A and B across medium m

$$\text{Interaction} = -\frac{A_{\text{Hamaker}}(l)}{12\pi l^2} \quad A_{\text{Ham}}(l) = \frac{3kT}{2} \sum_{\substack{\text{Matsubara sampling} \\ \text{frequencies } \xi_n}} \left( \frac{\epsilon_A - \epsilon_m}{\epsilon_A + \epsilon_m} \right) \left( \frac{\epsilon_B - \epsilon_m}{\epsilon_B + \epsilon_m} \right) \times \text{Rel}(l)$$

Sum over entire frequency spectrum!

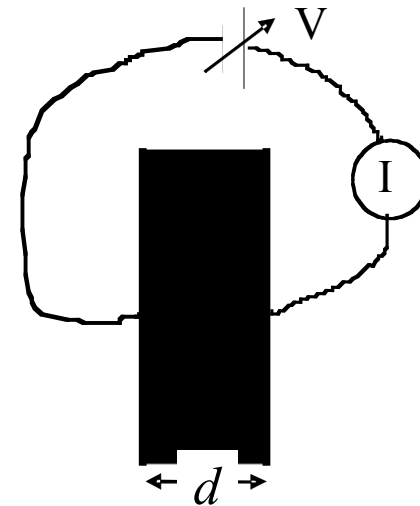
Differences in the  
responses of materials  
creates the force.



Epsilons  $\epsilon_A$ ,  $\epsilon_B$ ,  $\epsilon_m$ , for interaction come from noise!

$$\langle I^2 \rangle_\omega = \frac{4kT}{R} \quad (\text{traditional, Nyquist, Johnson})$$

$$\langle I^2 \rangle_\omega = \frac{\hbar\omega}{2\pi} \coth\left(\frac{\hbar\omega}{2kT}\right) \frac{\omega\epsilon''(\omega)}{4\pi d} \quad (\text{modern})$$



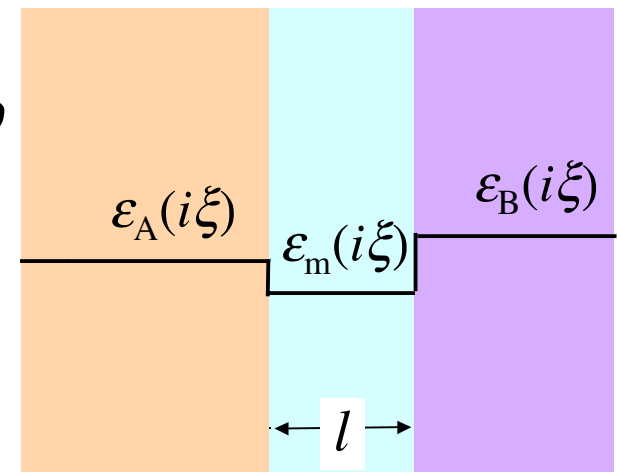
Recall the dissipation term  $\epsilon''(\omega)$  in  
 $\epsilon(\omega) = \epsilon'(\omega) + i\epsilon''(\omega)$ .

Use the Kramers-Kronig transform

For “imaginary frequency”

$$\epsilon(i\xi) \equiv 1 + \frac{2}{\pi} \int_0^\infty \frac{\omega \epsilon''(\omega)}{\omega^2 + \xi^2} d\omega$$

$$\xi = \xi_n \equiv \frac{2\pi kT}{\hbar} n, \quad n = 0, 1, 2, \dots$$



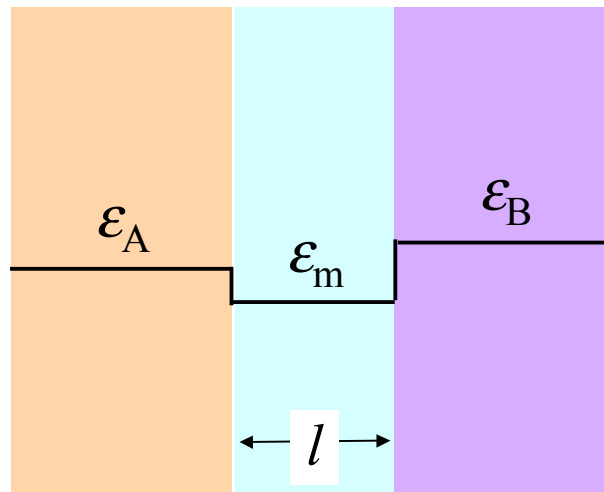
# Van der Waals forces (Lifshitz): half-spaces A and B across medium m

$$G_{\text{AmB}}(l) = -\frac{A(l)}{12\pi l^2}$$

$$A(l) = \frac{3kT}{2} \sum_{\text{Matsubara sampling frequencies } \xi_n} \left( \frac{\epsilon_A - \epsilon_m}{\epsilon_A + \epsilon_m} \right) \left( \frac{\epsilon_B - \epsilon_m}{\epsilon_B + \epsilon_m} \right) \times R_{\text{relativity}}(l)$$

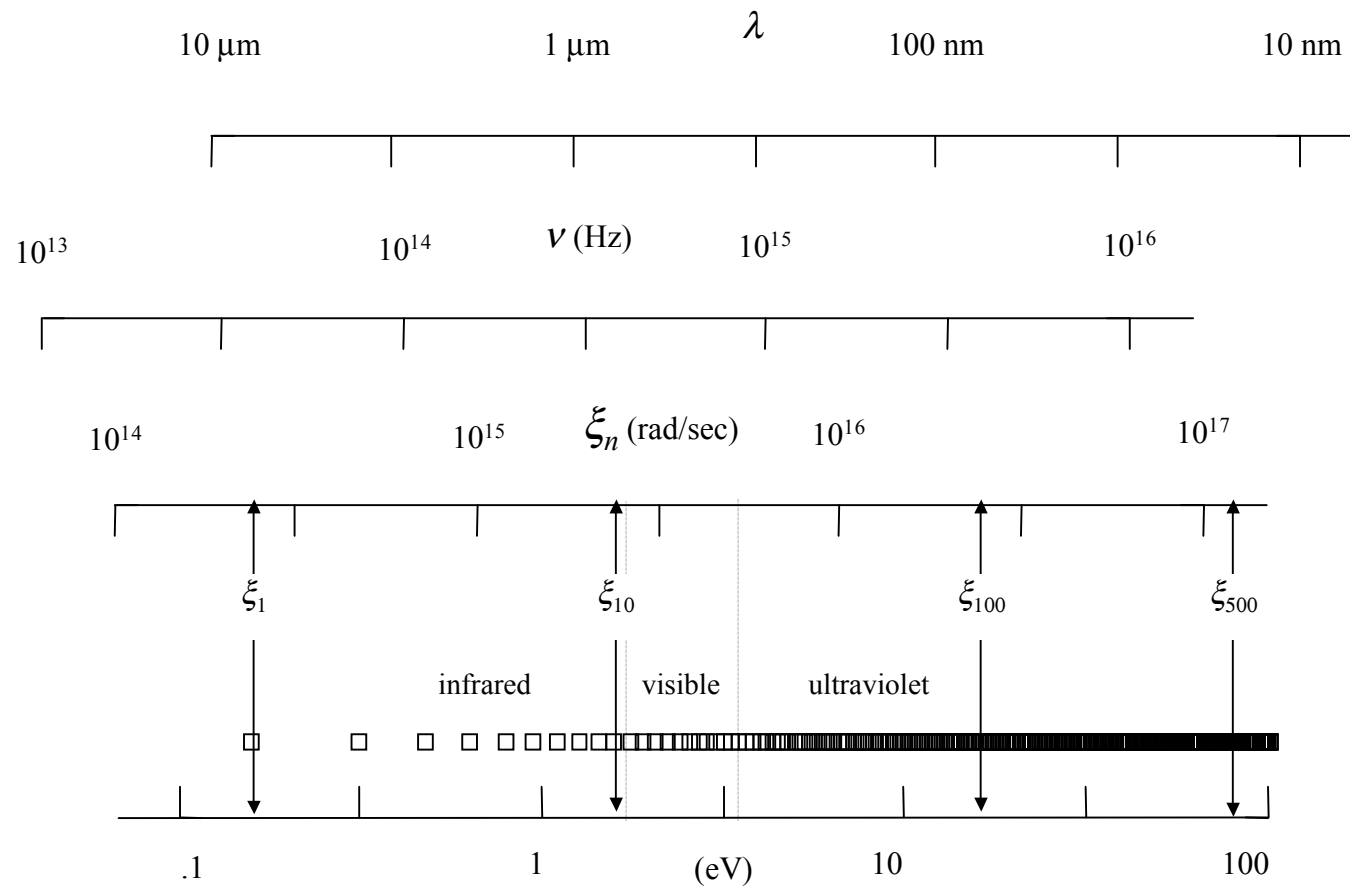
$$\epsilon_i = \epsilon_i(i\xi_n)$$

Dielectric  
response



$$\hbar \xi_n \equiv 2\pi kTn$$

# Matsubara frequencies at $T_{\text{room}}$ , as $\lambda$ , $\nu$ , and $\xi_n = 2\pi\nu$



The first sampling frequency after  $\xi_0 = 0$ , corresponds to IR vibrations.

$$l_1 = 2\pi c / \xi_1 = 7.82 \times 10^{-4} \text{ cm} = 7.82 \text{ mm} = 7.82 \times 10^4 \text{ Angstroms.}$$

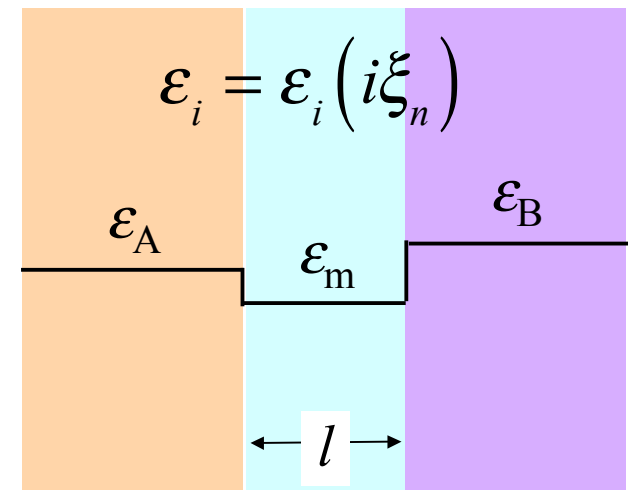
## Lifshitz et al.: half-spaces A and B across medium m

$$G_{\text{AmB}}(l) = -\frac{A(l)}{12\pi l^2} \quad A(l) = \frac{3kT}{2} \sum_{\text{Matsubara sampling frequencies } \xi_n} \left( \frac{\epsilon_A - \epsilon_m}{\epsilon_A + \epsilon_m} \right) \left( \frac{\epsilon_B - \epsilon_m}{\epsilon_B + \epsilon_m} \right) \times R_n(l)$$

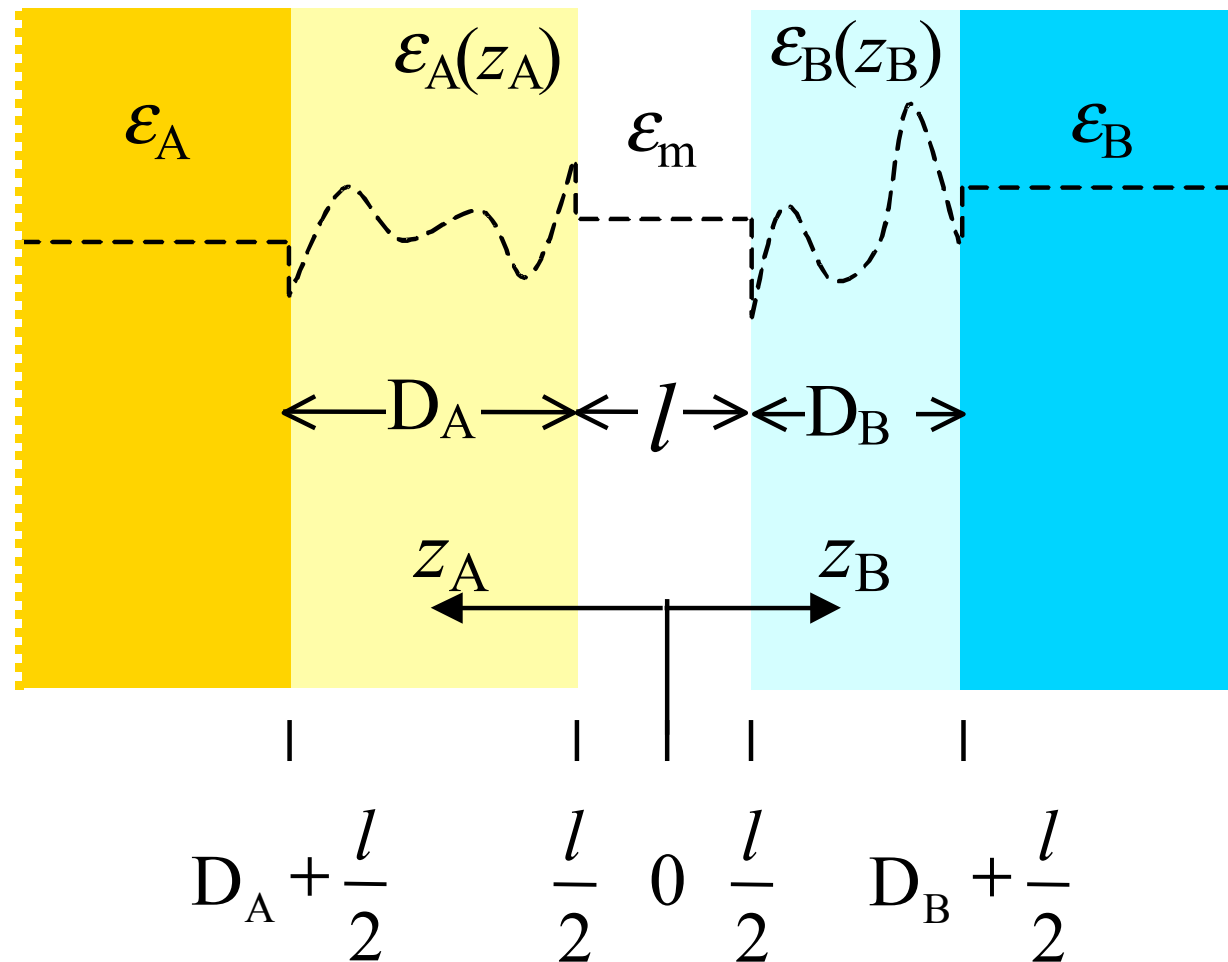
$$\hbar \xi_n \equiv 2\pi k T n \quad R_n \approx (1 + r_n) e^{-r_n}$$

$$r_n = \left( \frac{2l}{c} \right) / \left( \frac{1}{\xi_n} \right) = \frac{2l}{\lambda_T} n; \quad \lambda_T \equiv \frac{\hbar c}{2\pi k_B T_{\text{room}}} = 1.2 \mu\text{m}$$

$l =$	100 nm	1 $\mu\text{m}$	10 $\mu\text{m}$
$n: r_n = 1$	$n = 6$	$n = .6$	$n \ll 1$
$r_1 =$	.16	1.6	16
$R_1 =$	$\sim 1$	$< 1/2$	zero!



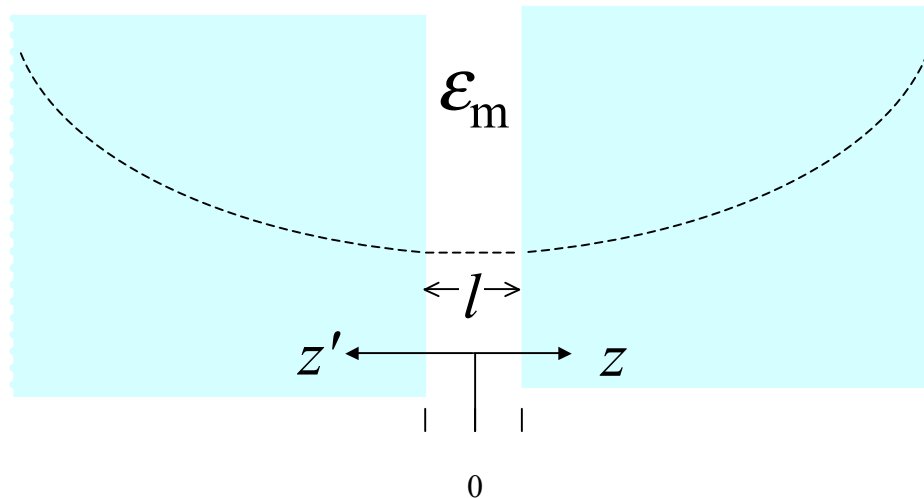
## Generalization for spatially varying polarizability $\varepsilon(z)$



E.g., Exponential variation of response in an infinitely thick layer

$$\varepsilon_{a'}(z') = \varepsilon_m e^{-\gamma_e(z' - l/2)}$$

$$\varepsilon_a(z) = \varepsilon_m e^{-\gamma_e(z - l/2)}$$



Small  $\gamma_e l$  limit

$$G(\gamma_e l \rightarrow 0) \sim \frac{kT\gamma_e^2}{32\pi} \sum_{n=0}^{\infty} \gamma_e^2 \ln(\gamma_e l)$$

George Weiss & VAP 1970's

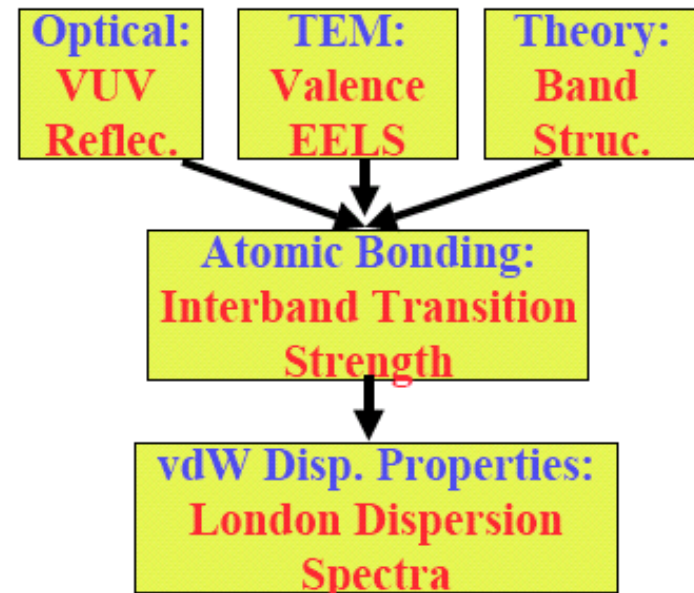
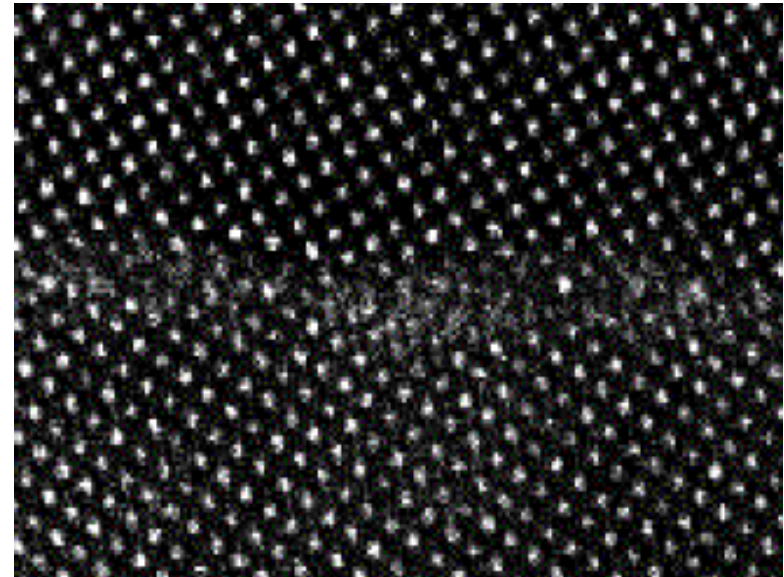
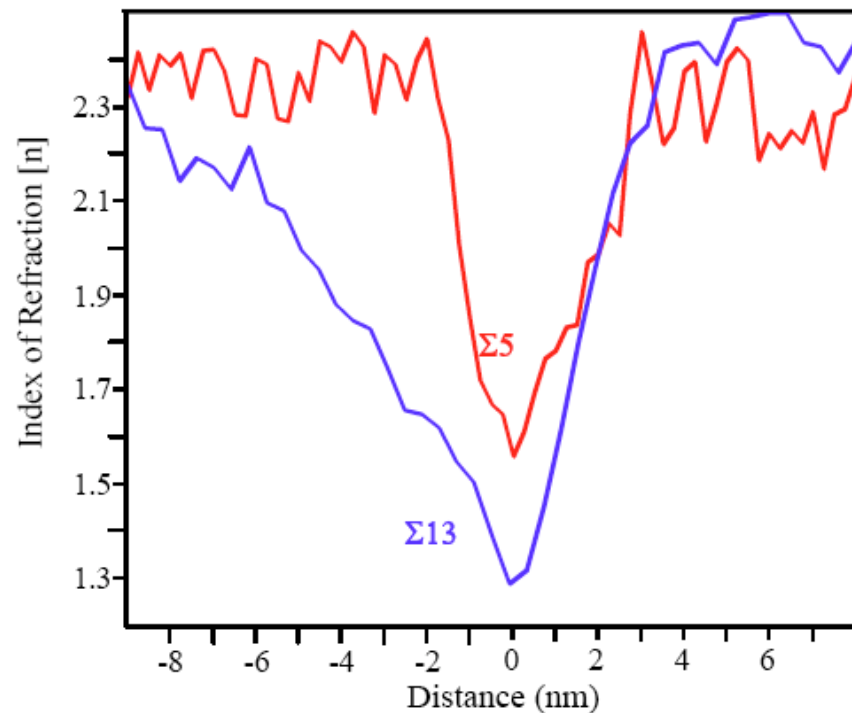


Bonus: Computer chip design

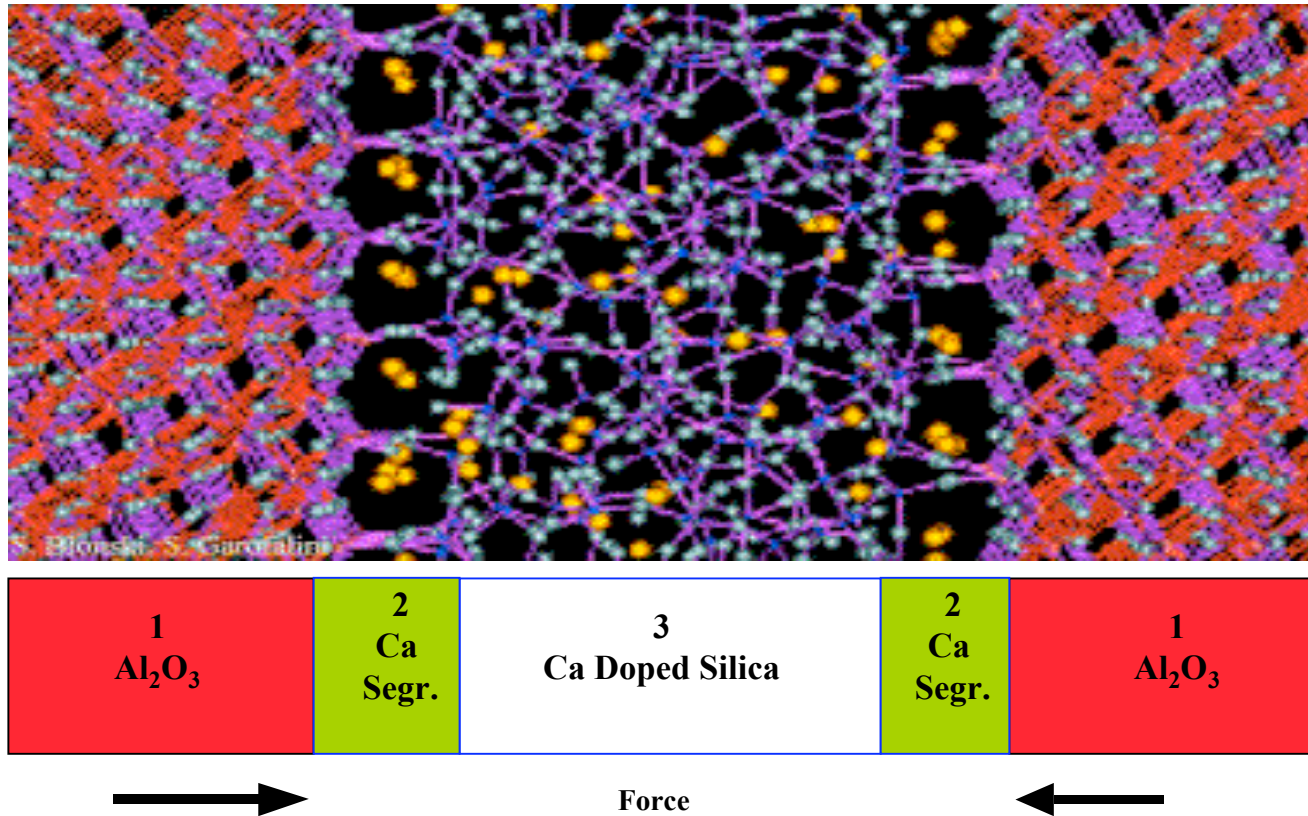
# Measure $\epsilon(z)$ !

SrTiO<sub>3</sub> vdW interaction across grain boundaries.

Roger French, Klaus van Benthem, Lin Desnoyers et al.



# Interfacial Adsorption, Segregation, Diffuse Layers



## Ca Doped Silica IGF in Alumina

Calcium Segregation To Interface (Garofalini – Rutgers)

As A Function of Ca Conc.

Extra Shielding Layer For Dispersion Interaction

(from Roger French 2004)

# Practical, profitable, instructive

- Production of thin film resistors
- ~ 300 in every desk/laptop computer
- Spectroscopy
  - to stimulate theory and
  - to examine new systems

## DLP vis a vis Casimir

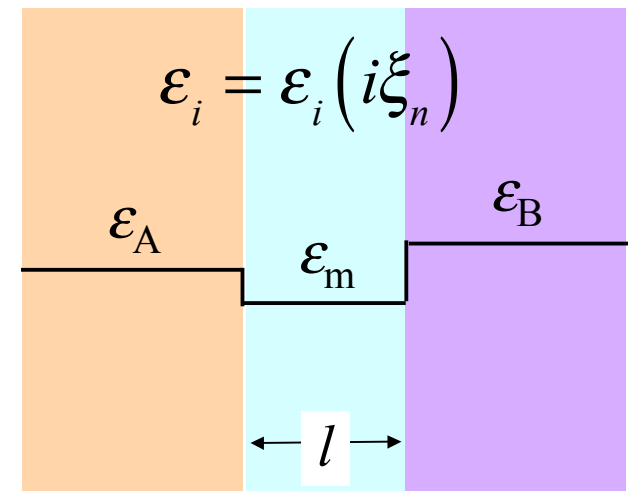
$$G_{\text{AmB}}(l) = -\frac{A(l)}{12\pi l^2} \quad A(l) = \frac{3kT}{2} \sum_{\text{Matsubara sampling frequencies } \xi_n} \left( \frac{\epsilon_A - \epsilon_m}{\epsilon_A + \epsilon_m} \right) \left( \frac{\epsilon_B - \epsilon_m}{\epsilon_B + \epsilon_m} \right) \times R_n(l)$$

$$\hbar \xi_n \equiv 2\pi kT n \quad R_n \approx (1 + r_n) e^{-r_n}$$

$$r_n = \left( \frac{2l}{c} \right) / \left( \frac{1}{\xi_n} \right) = \frac{2l}{\lambda_T} n; \quad \lambda_T \equiv \frac{\hbar c}{2\pi k_B T_{\text{room}}} = 1.2 \mu\text{m}$$

Casimir (“T = 0 K”)

$$G_{\text{Casimir}}(l) \approx -\frac{\hbar c \pi^2}{720 l^3}; \quad P_{\text{Casimir}}(l) \approx -\frac{\hbar c \pi^2}{240 l^4}$$

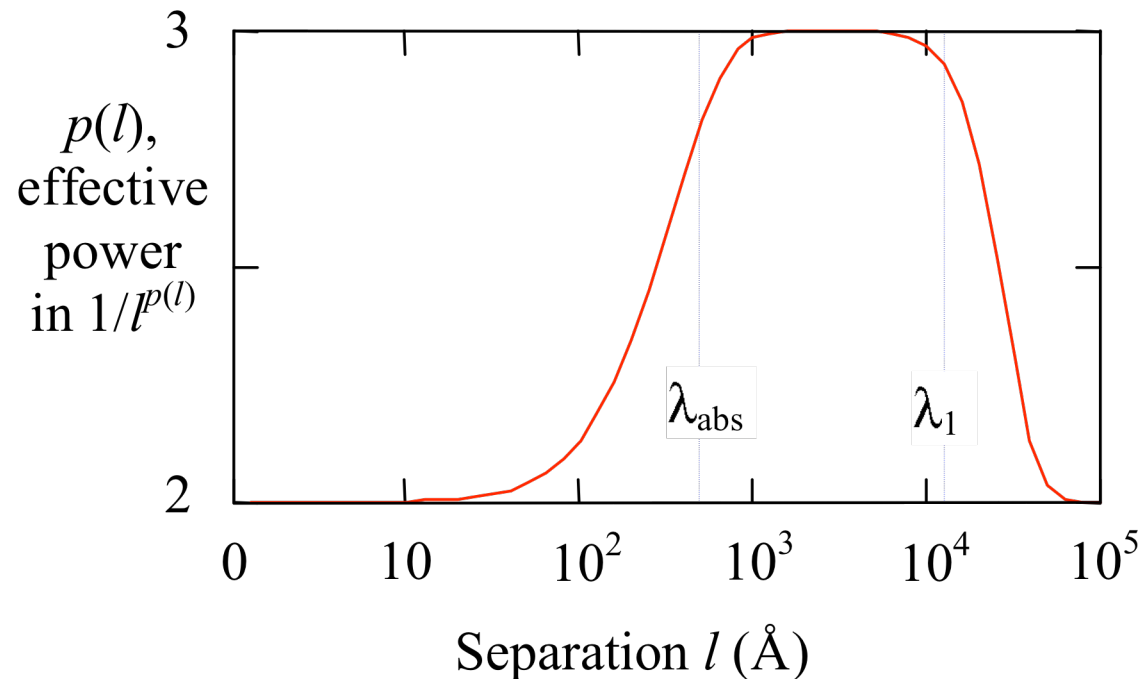


“Power law” from a single-oscillator,

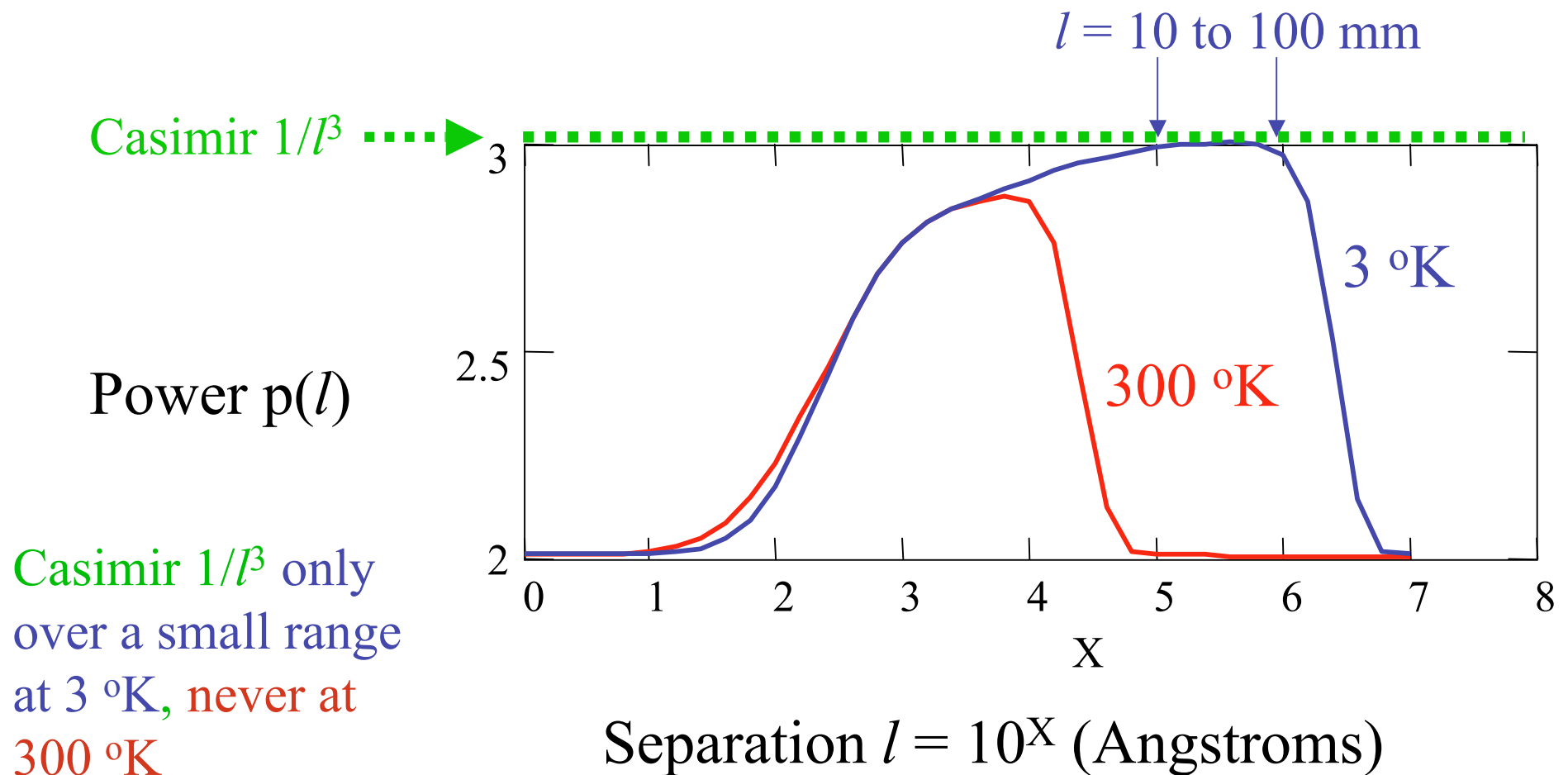
$$\lambda_{\text{absorption}} = 500 \text{ Angstrom},$$

$$\epsilon_{\text{left}} = \epsilon_{\text{right}} \text{ across vacuum}$$

$$G_{\text{AmB}}(l) = -\frac{A_{\text{Am/Bm}}(l)}{12\pi l^2} \quad p(l) = -\frac{d \ln(G_{\text{AmB}}(l))}{d \ln(l)}$$



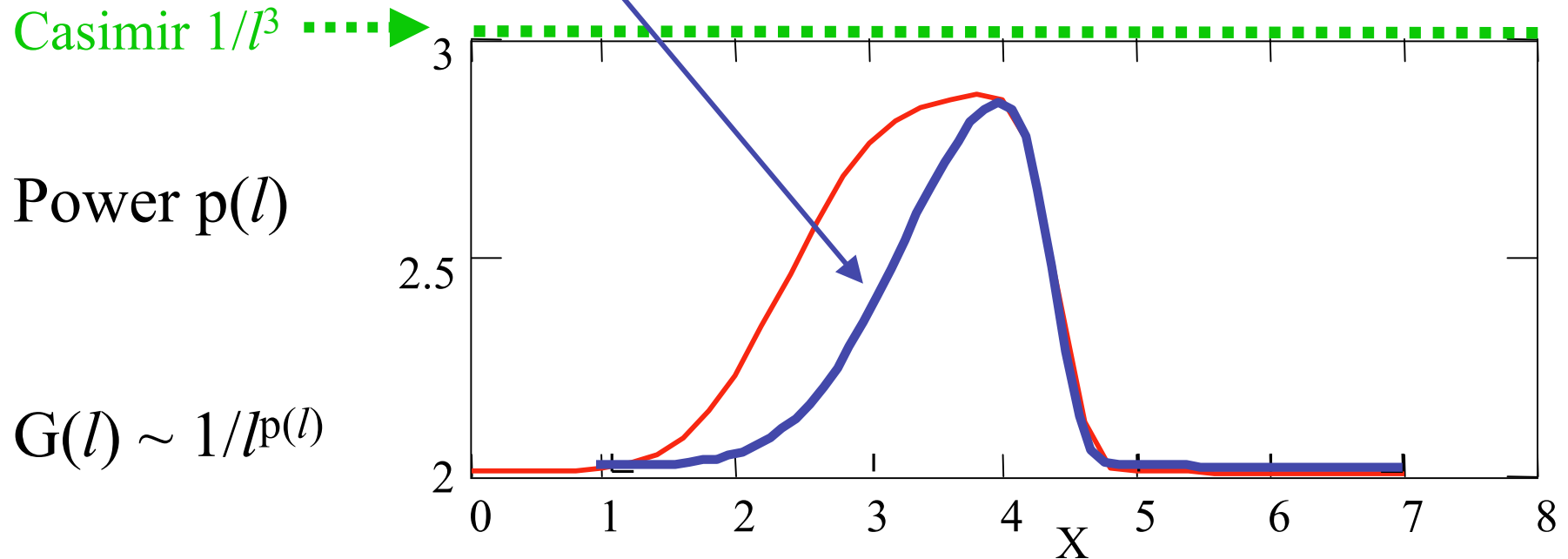
Effective power  $p(l)$ , interaction energy  $G(l) \sim 1/l \ p(l)$   
 Gold to gold, across vacuum, 3 °K and 300 °K



Using all four dielectric terms from Table L2.4.1, Parsegian, Van der Waals Forces, Cambridge Univ Press, 2006. Computation made with Rudi Podgornik.

Gold across vacuum

300 °K, **with** and **without** non-conduction terms in dielectric;  
**with conduction term only, see even less “Casimir”  $1/l^3$  variation**



Separation  $l = 10^X$  (Angstroms)

Omission of the finite-frequency absorption frequency terms makes it even harder for the power to reach 3.

Computations use **all four dielectric terms** vs. **conduction term only**  
(Table L2.4.1, Parsegian, Van der Waals Forces, 2006)



Two metals in vacuum at  $T_{\text{room}}$   $l \sim 10 \mu\text{m}$ , never Casimir

$$A(l) = \frac{3kT}{2} \sum_{\text{Matsubara sampling frequencies } \xi_n} \left( \frac{\epsilon_A - \epsilon_m}{\epsilon_A + \epsilon_m} \right) \left( \frac{\epsilon_B - \epsilon_m}{\epsilon_B + \epsilon_m} \right) \times R_n(l) \rightarrow \frac{3kT}{4}$$

$$G(l) \approx -\frac{A(l)}{12\pi l^2} = -\frac{3kT}{48\pi l^2} = -\frac{kT}{16\pi l^2} \quad \text{without magnetic terms}$$

$$G(l) \approx -\frac{3kT}{24\pi l^2} \zeta(3) = -\frac{kT}{8\pi l^2} \zeta(3) \quad \text{with magnetic terms, and proper summation}$$

$$\text{vs. Casimir (T = 0 K)} \quad G_{\text{Casimir}}(l) \approx -\frac{\hbar c \pi^2}{720 l^3}; \quad P_{\text{Casimir}}(l) \approx -\frac{\hbar c \pi^2}{240 l^4}$$

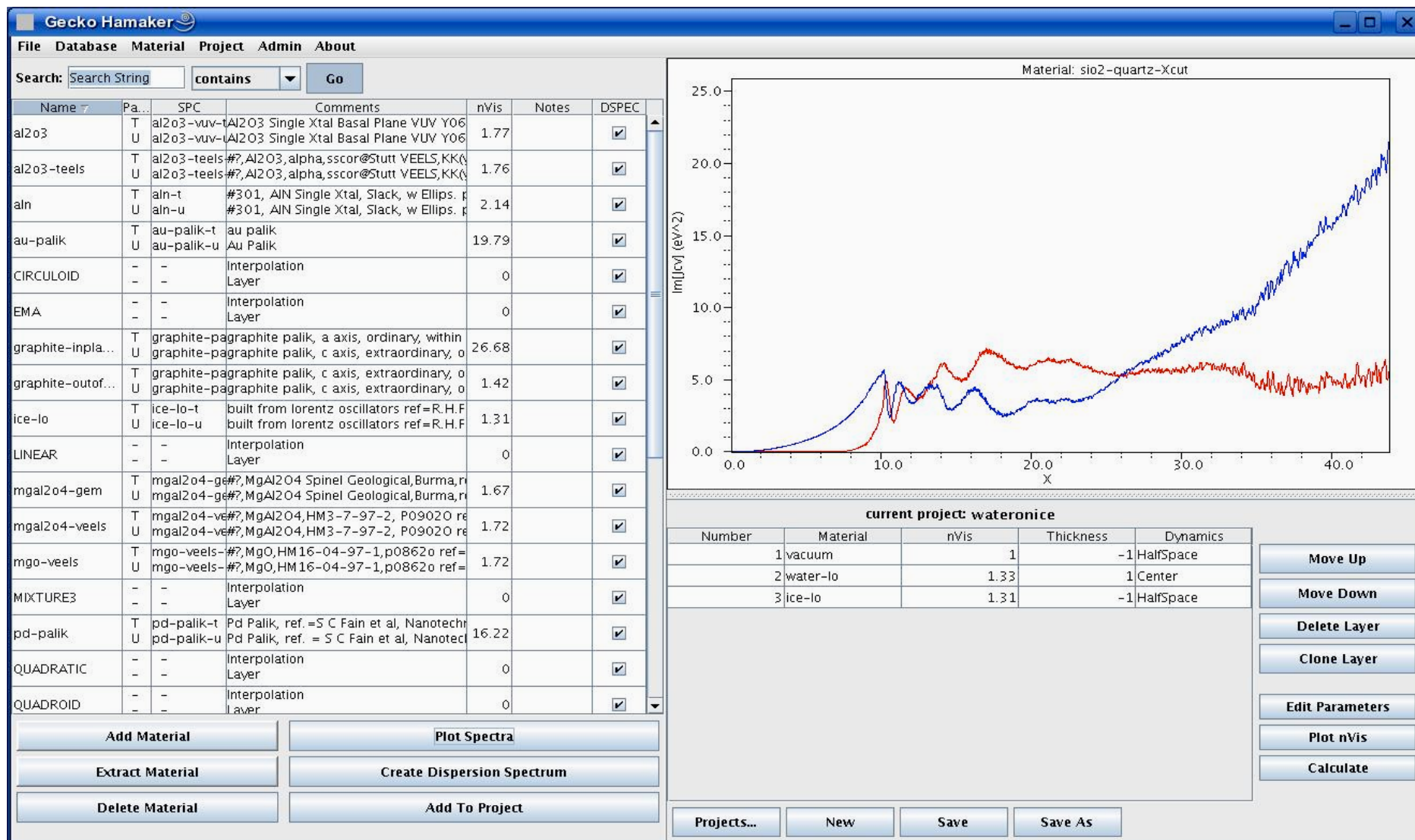
Stick to DLP-style full solutions

tabulate formulae and spectra

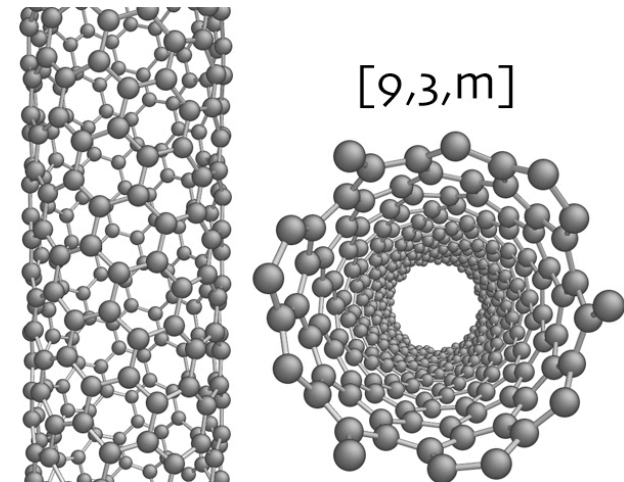
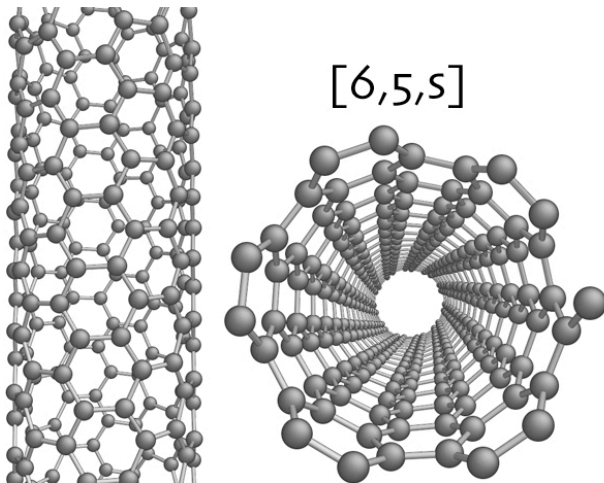
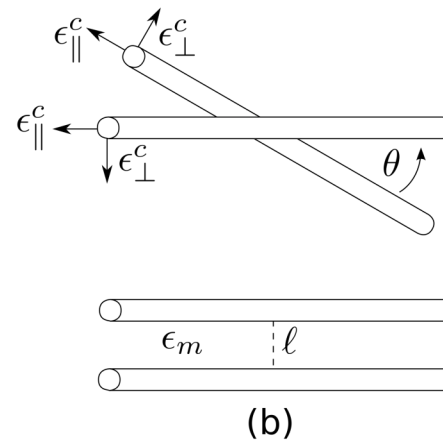
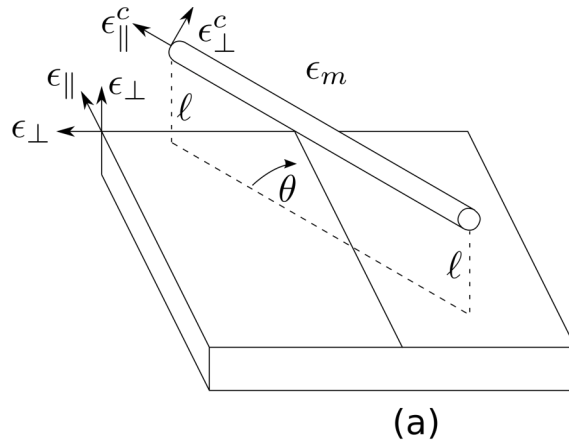
# Gecko Hamaker: Open Source Hamaker Program

- Full Spectral, Retarded Hamaker, Coefficients

<http://geckoproj.sourceforge.net/>; Lin Desnoyer, Roger French

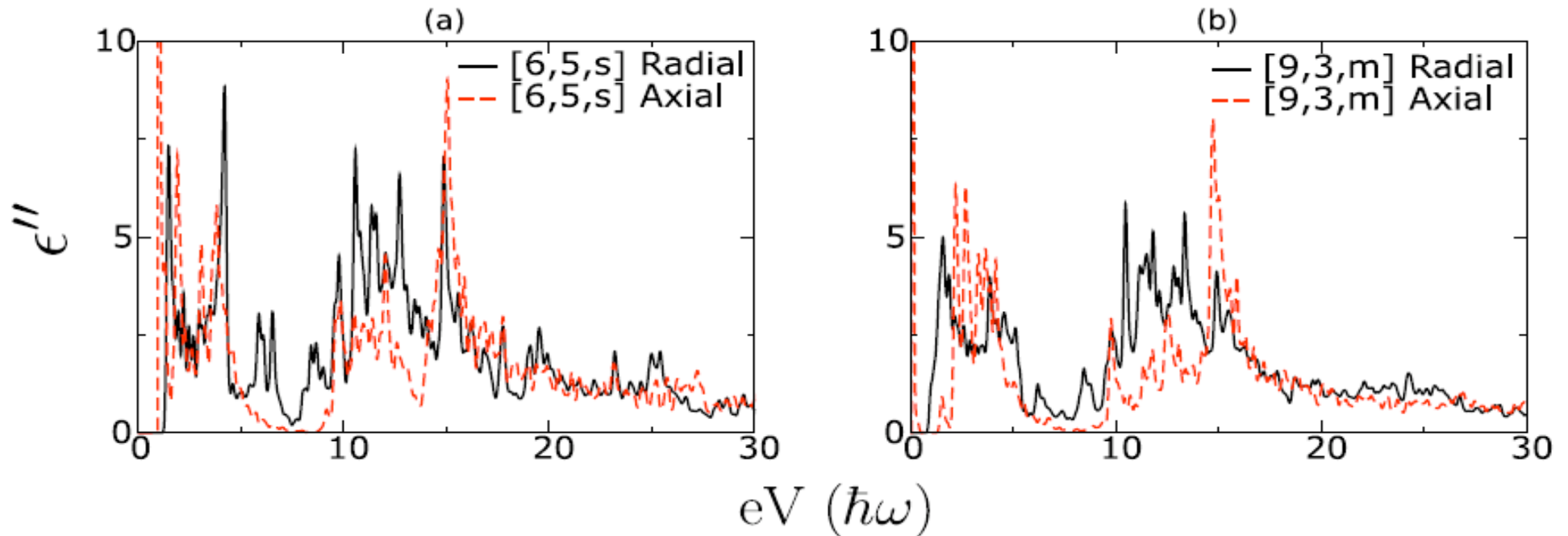


# Chirality Dependent van der Waals – London Dispersion Interactions of Carbon Nanotube Systems.



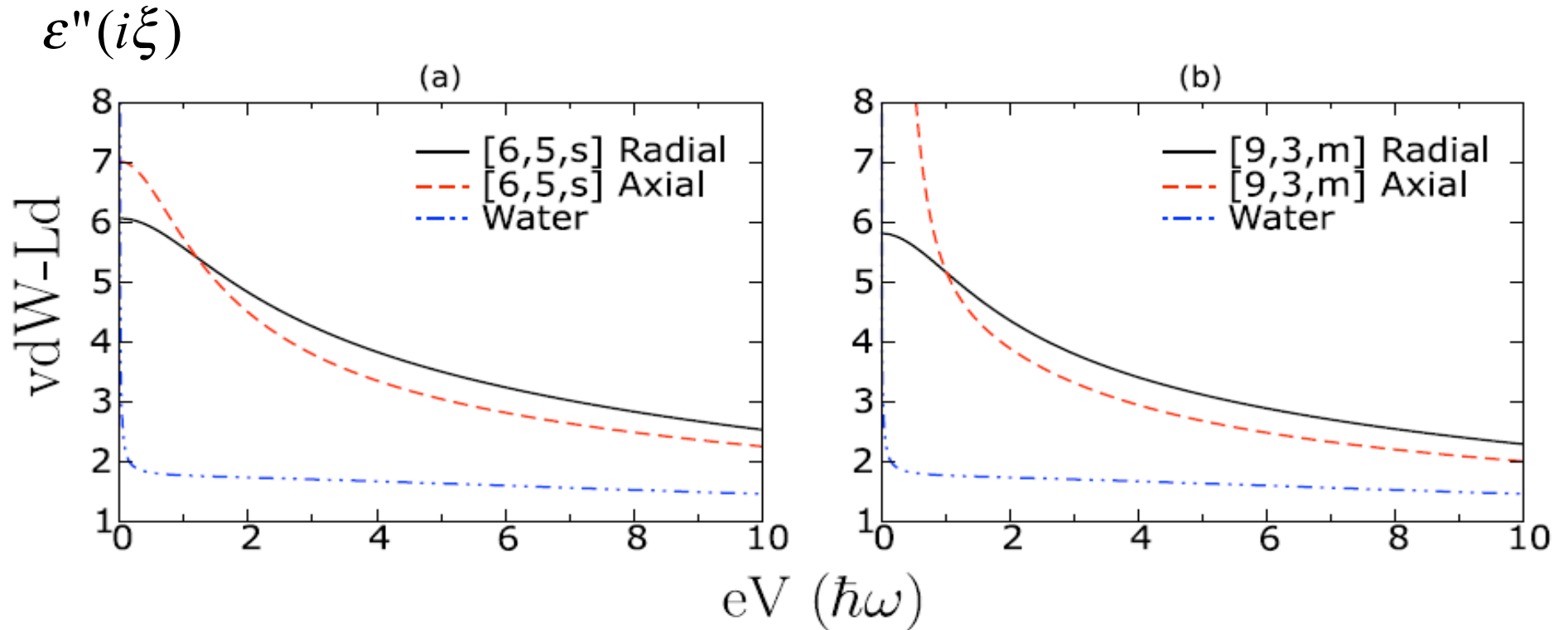
Rick Rajter, Roger French, Wai-Yim Ching, Rudi Podgornik, VAP

# Uniaxial Optical Properties Of [6,5,s] & [9,3,m] SWCNT



- Radial Directions Have Similar Properties
- Axial Directions Very Different
  - Due To Metallic Axial Property Of [9,3,m]

# London Disp. Spectra Of [6,5,s] & [9,3,m] CNTs



- Water vdW-Ld Spectrum Max of 78 at 0 eV
- [9,3,m] Peaks of 333 at 0 eV

# Optically Anisotropic vdW-Ld Formalism

$$G(\ell, \theta) = -\frac{\mathcal{A}^{(0)} + \mathcal{A}^{(2)} \cos^2 \theta}{12\pi\ell^2}$$

$$\mathcal{A}^{(0)} = \frac{3}{2}k_B T \sum_{n=0}^{\infty} \frac{1}{2\pi} \int_0^{2\pi} \Delta_{\mathcal{L}m}(\phi) \Delta_{\mathcal{R}m}(\phi - 90) d\phi$$

$$\mathcal{A}^{(0)} + \mathcal{A}^{(2)} = \frac{3}{2}k_B T \sum_{n=0}^{\infty} \frac{1}{2\pi} \int_0^{2\pi} \Delta_{\mathcal{L}m}(\phi) \Delta_{\mathcal{R}m}(\phi) d\phi$$

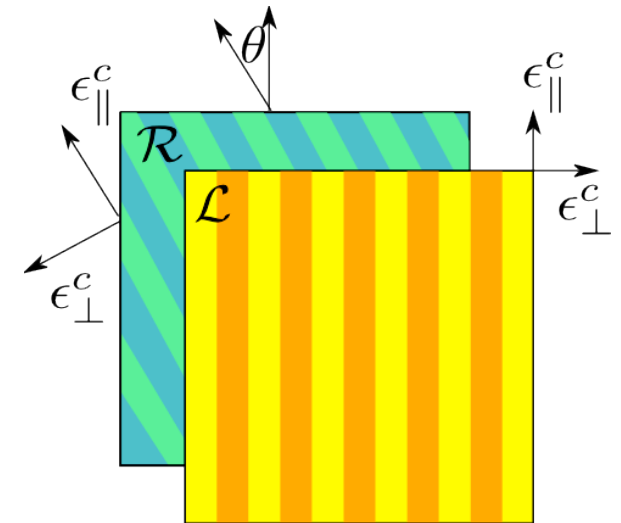
$$\Delta_{\mathcal{L}m}(\phi) = \left( \frac{\epsilon_{\perp}(\mathcal{L}) \sqrt{1 + \gamma(\mathcal{L}) \cos^2 \phi} - \epsilon_m}{\epsilon_{\perp}(\mathcal{L}) \sqrt{1 + \gamma(\mathcal{L}) \cos^2 \phi} + \epsilon_m} \right)$$

$$\Delta_{\mathcal{R}m}(\phi) = \left( \frac{\epsilon_{\perp}(\mathcal{R}) \sqrt{1 + \gamma(\mathcal{R}) \cos^2 \phi} - \epsilon_m}{\epsilon_{\perp}(\mathcal{R}) \sqrt{1 + \gamma(\mathcal{R}) \cos^2 \phi} + \epsilon_m} \right)$$

$$\Delta_{\mathcal{R}m}(\phi - 90) = \left( \frac{\epsilon_{\perp}(\mathcal{R}) \sqrt{1 + \gamma(\mathcal{R}) \sin^2 \phi} - \epsilon_m}{\epsilon_{\perp}(\mathcal{R}) \sqrt{1 + \gamma(\mathcal{R}) \sin^2 \phi} + \epsilon_m} \right)$$

$$\gamma = \frac{\epsilon_{\parallel} - \epsilon_{\perp}}{\epsilon_{\perp}}$$

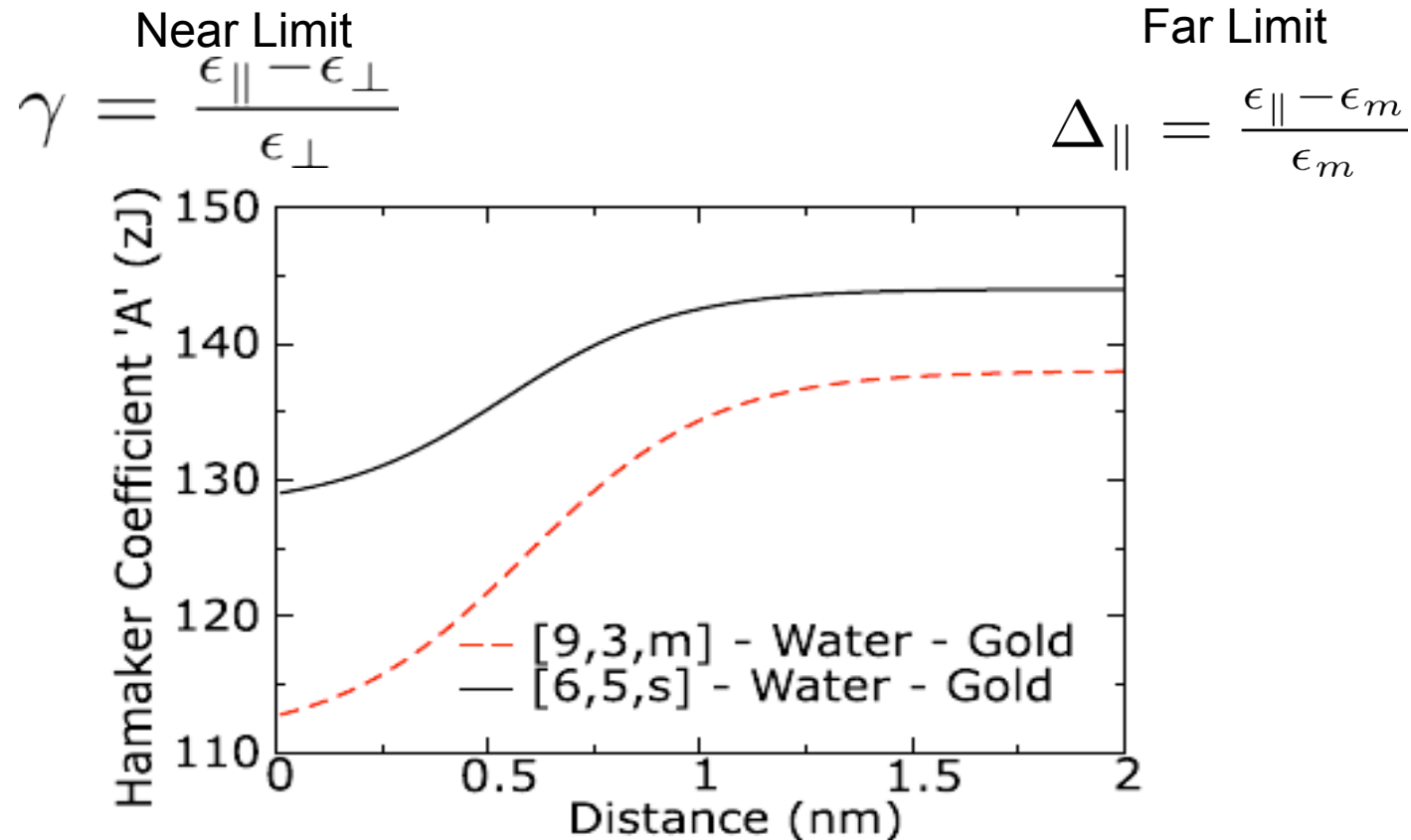
- $\mathcal{A}^{(0)}$  Is Rotation Independent Part:  $f(l)$
- $\mathcal{A}^{(2)}$  Is Rotation Dependent Part:  $f(\theta)$ 
  - Of vdW-Ld Interaction



(b)

- Example:  $A_{123}$  Non-retarded
  - Uniaxial Optical Properties
- $\Delta$  Is Optical Contrast
  - With Interlayer Medium
- $\gamma$   $\gamma$  Is Optical Anisotropy
  - Of Material
- Torques Due To  $\gamma$ 
  - In Addition To Normal Forces

# Hamaker Coefficients Versus distance

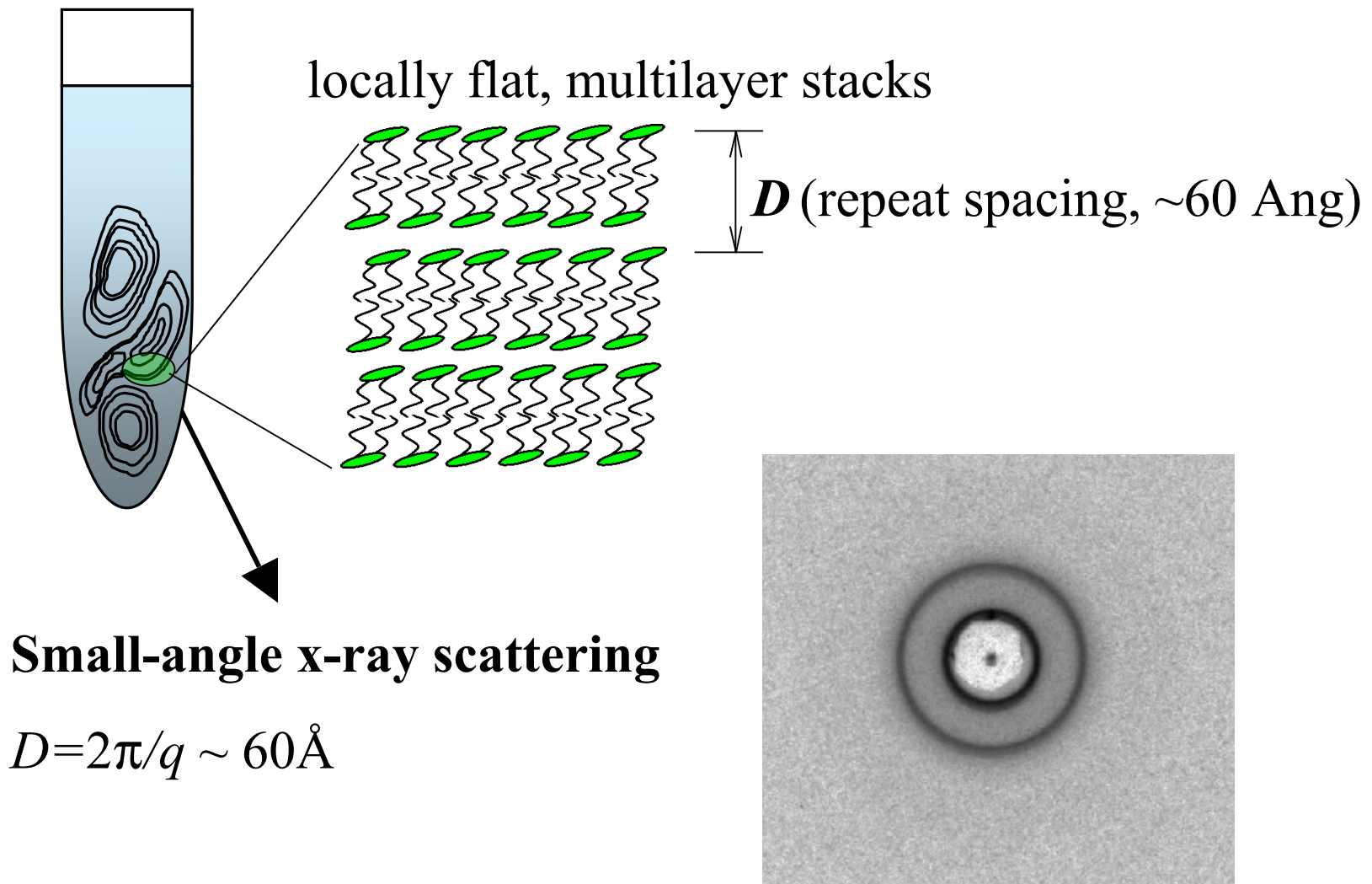


- Near Limit Is < 2 Diameters, And Far Limit Is > 2 Diameters
- Semiconducting CNT's Hamaker Coefficient Larger Than Metallic
- Far Limit Hamaker Coeff.s Larger Than Near Limit
  - Due To  $\Delta$  parallel



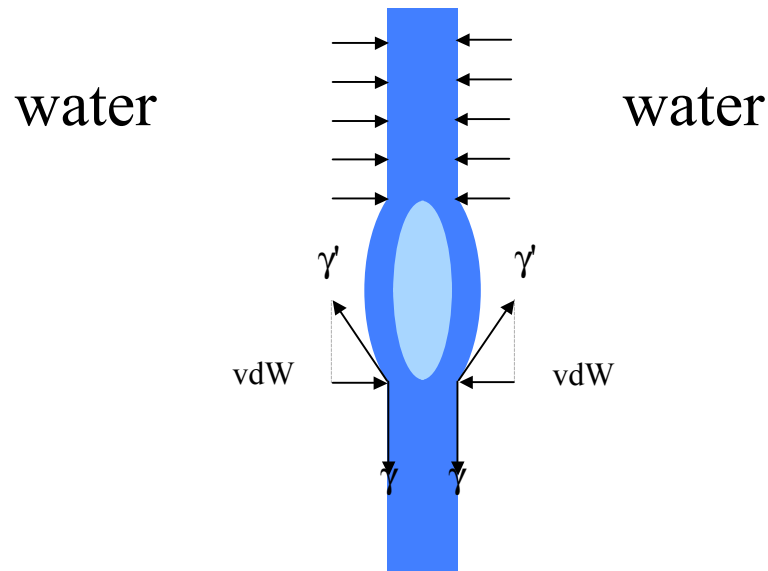
# Lipid bilayers

# Multilayers: Neutral lipid bilayers in salt water



H. Petrache, D. Harries, I. Kimche, J. Nagle, S. Tristram-Nagle, et al.

## Forces across bilayers (Haydon & Taylor, 1968)



Hydrocarbon  
membrane

~ 4 nm thick layer  
with trapped hc drop

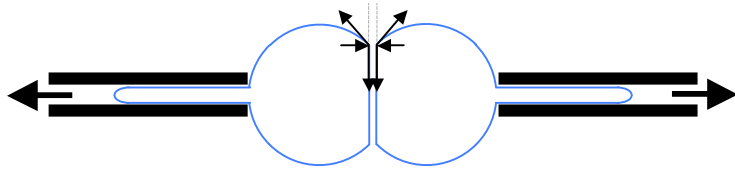
By the strength with which they flatten against each other, two juxtaposed bilayers create a measurable contact angle.

D. A. Haydon & J. L. Taylor,  
"Contact angles for thin lipid films  
and the determination of London-van  
der Waals forces" *Nature*, 217: 739 -  
740 (1968)

Parsegian, V.A, Ninham B.W.:  
Application of the Lifshitz theory to  
the calculation of van der Waals  
forces across thin lipid films. *Nature*  
224: 1197-1198 (1969)

# Forces between bilayer vesicles (Evan Evans, Peter Rand)

Water inside and outside



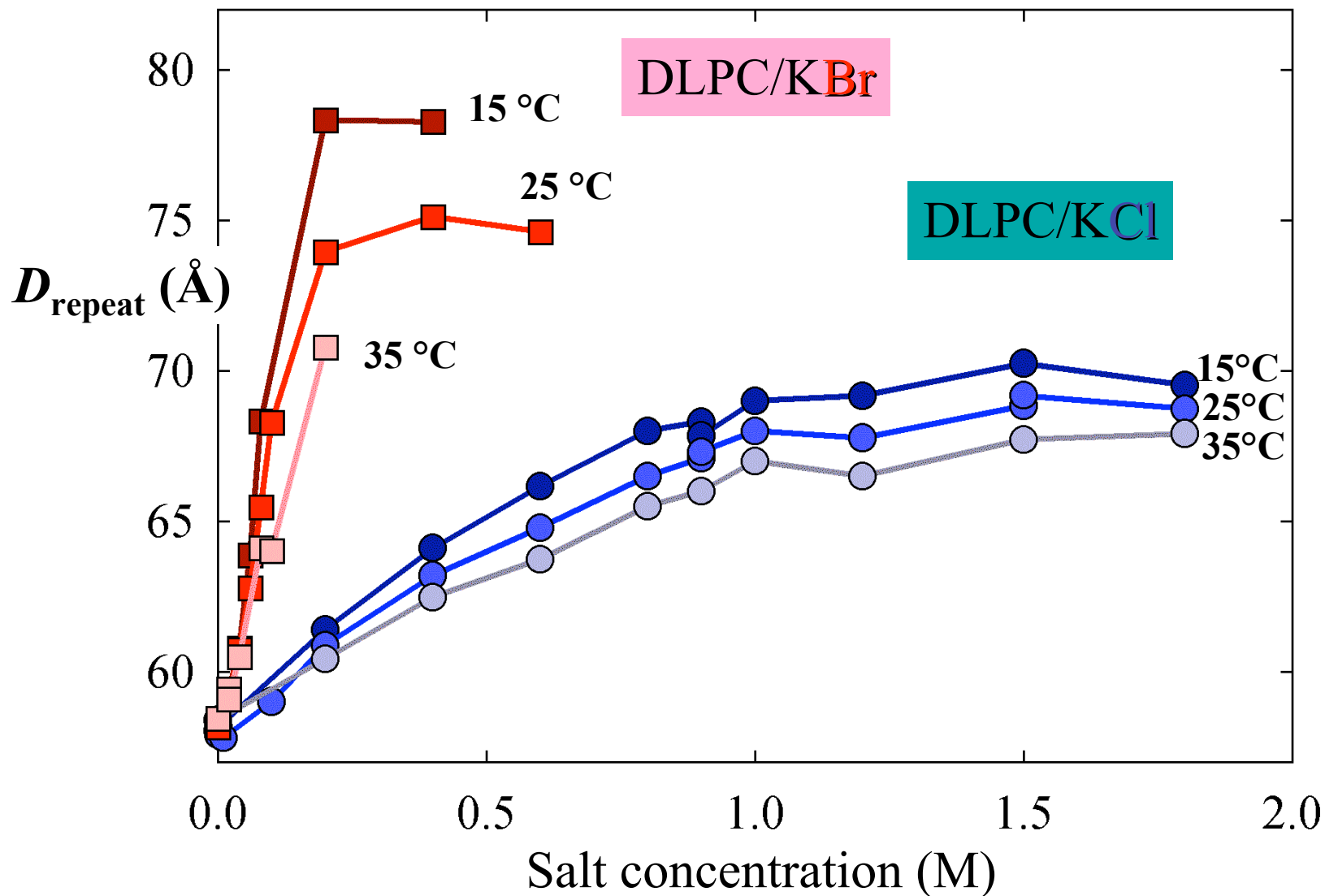
Suck on vesicles with pipettes

In practice, van der Waals forces appear mixed with lamellar motions as well as with repulsive hydration forces.

E. A. Evans, "Entropy-driven tension in vesicle membranes and unbinding of adherent vesicles" *Langmuir*, 7:1900-1908 (1991)

In excess solution, neutral lipids swell with added salt.

Horia Petrache et al (2006)



## Salt screening/weakening of vdW forces: three new ideas

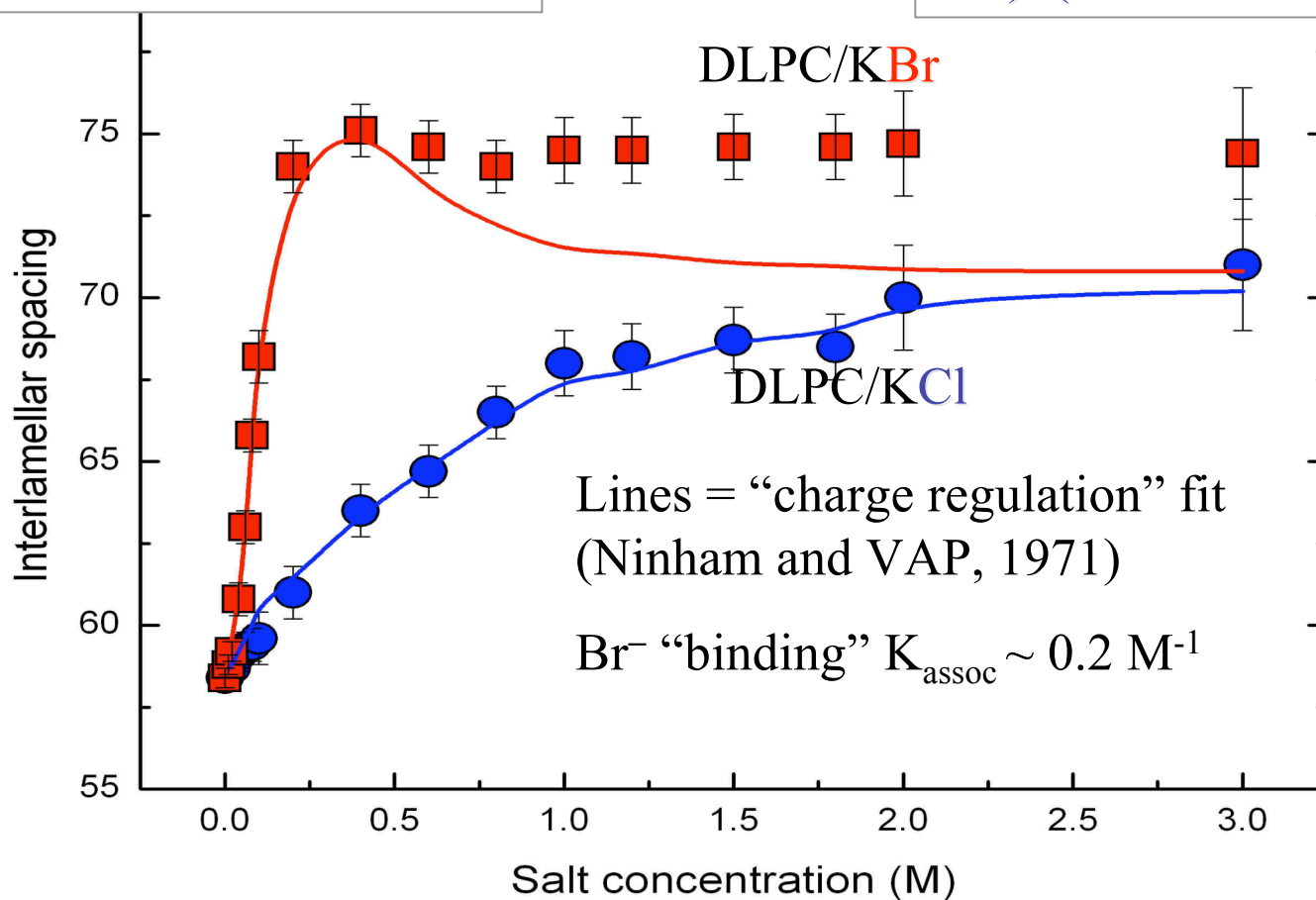
H. I. Petrache, S. Tristram-Nagle, D. Harries, N. Kucerka, J. F. Nagle, V. A. P., Swelling of phospholipids by monovalent salt J. Lipid Res. 47, 302-309 (2006)

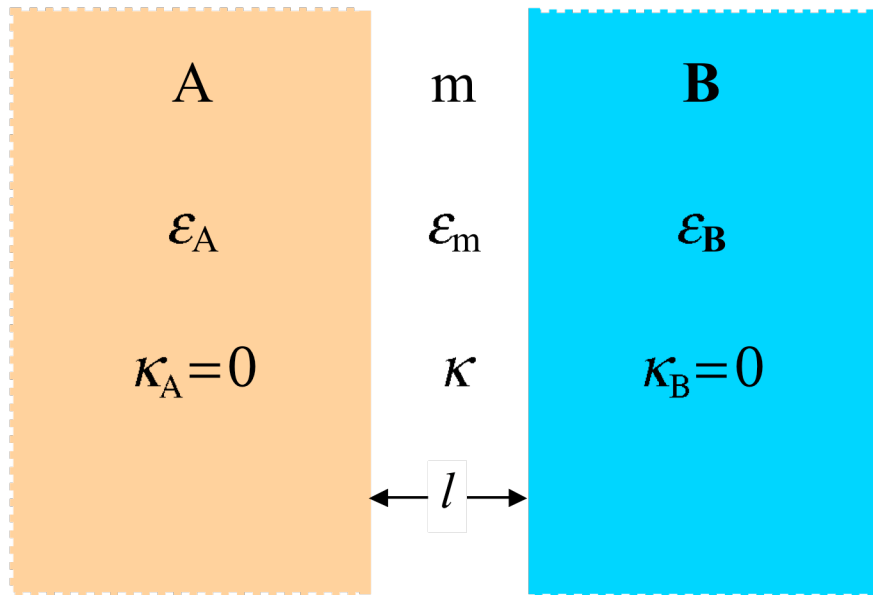
### Low salt:

- \*screening of zero frequency vdW attraction (Ninham & VAP)
- \*electrostatic repulsion from Br binding via vdW forces (Ninham)

### High salt:

- \* vdW weakening at optical frequencies (refractive index of salt solutions increases with salt). (Rand & VAP)





“double  
screening”  
of low  
frequency  
fluctuation  
forces

or  $2\kappa l \gg 1$ ,

$$G_{\text{AmB}}(l) \approx -\frac{kT}{16\pi l^2} \bar{\Delta}_{\text{Am}} \bar{\Delta}_{\text{Bm}} (1 + 2\kappa l) e^{-2\kappa l}$$

$$= -\frac{kT}{16\pi l^2} \bar{\Delta}_{\text{Am}} \bar{\Delta}_{\text{Bm}} \left(1 + 2l/\lambda_D\right) e^{-2l/\lambda_D} = -\frac{kT}{16\pi l^2} \bar{\Delta}_{\text{Am}} \bar{\Delta}_{\text{Bm}} R_0$$

$$\text{Ionic screening factor } R_0 = (1 + 2\kappa l) e^{-2\kappa l} = \left(1 + 2l/\lambda_D\right) e^{-2l/\lambda_D} \leq 1$$

$$\bar{\Delta}_{\text{Lm}} \equiv \left( \frac{\epsilon_L - \epsilon_m}{\epsilon_L + \epsilon_m} \right), \quad \bar{\Delta}_{\text{Rm}} \equiv \left( \frac{\epsilon_R - \epsilon_m}{\epsilon_R + \epsilon_m} \right).$$

Kevin Cahill:

How about first-order interactions?"

distance; cf. §02, PROBLEM 1, and §01, PROBLEM 1.

‡ This, of course, does not imply that the mean value of the interaction energy of the atoms is precisely zero. It diminishes exponentially with distance, i.e. more rapidly than every finite power of  $1/r$ , and hence each term of the expansion vanishes. This occurs because the expansion of the interaction operator in terms of the multipole moments involves the assumption that the charges of the two atoms are at a large distance  $r$  apart, whereas in quantum mechanics the electron density distribution has finite (though exponentially small) values even at large distances.

Landau & Lifshitz, Quantum Mechanics, footnote page 341



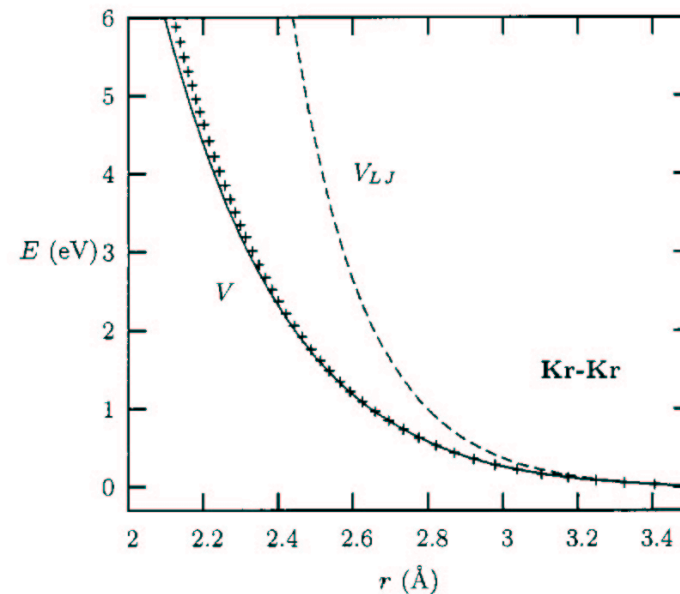
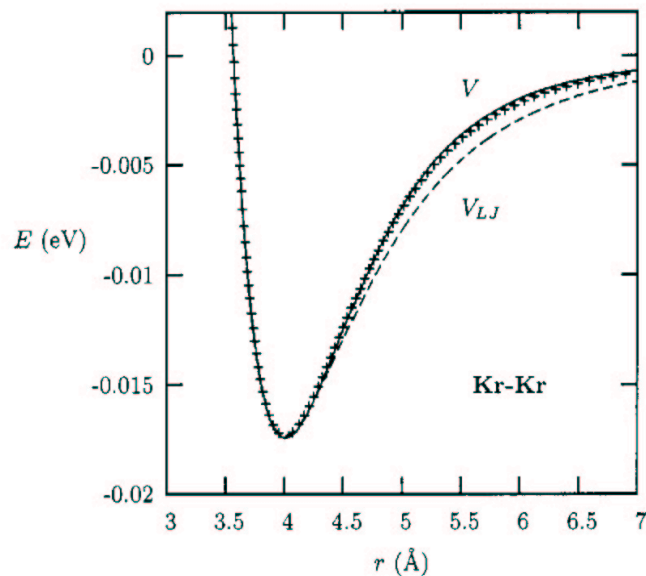
# First-order van der Waals forces atom-atom attraction

A Rydberg-like potential  $V_{\text{Rydberg}}$ ,

better than Lennard-Jones  $V_{\text{LJ}}$  6-12 potential generally used.

$$V_{\text{Rydberg}} = V(r) = ae^{-br} (1 - cr) - \frac{d}{r^6 + er^{-6}} \quad V_{\text{LJ}}(r) = |V(r_o)| \left[ \left( \frac{r_o}{r} \right)^{12} - 2 \left( \frac{r_o}{r} \right)^6 \right]$$

+ symbol “exact” numerical solution Meath and Aziz, Molec. Phys., 52, 225 (1984).



Kevin Cahill & VAP, J. Chem. Phys., 121:10839-42 (2004)

# strategy

Solve for more geometries and for real materials (pure Casimir is not questionable as an idea, but when does it really occur?)

Piece apart the “zero-frequency” term, still not well understood

(dominates at long distances, especially at room temperature)

(important with polar materials, always with water)

Control conditions of measurements

-- are we measuring what we think we are measuring?

(high vacuum for clean surfaces)

(optical data, on samples themselves, to go with measurement)

Aim: Design shapes and materials so as to craft forces

Talk with each other! Nicely!!

Thanks